

# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Process for Enhancing Lubricating Oils and Catalysts therefor

- We, GULF RESEARCH & DEVELOPMENT COMPANY of Gulf Building, 7th Avenue and Grant Street, Pittsburgh, Pennsylvania, United States of America, a corporation organized under the laws of the State of Delaware, one of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a process for enhancing crude lubricating oil stocks, and to a catalyst thereof.
- The upgrading of crude lubricating oil stocks in order to produce improved lubricating oils or lubricating oil base stocks by means of catalytic hydrogenation has previously been suggested in the art. Such previously suggested techniques have usually required the treatment of the crude lubricating oil stocks with hydrogen under conditions of elevated temperature and pressure while employing a catalyst comprising metalliferous hydrogenating components supported on a carrier having a substantial degree of cracking activity such as, for example, siliceous cracking carriers including among other silica-alumina having a cracking activity index from about 35 or 40 up to about 80.
- It previously has been proposed in our British Patent Specification No. 928,761 to produce lubricating oil by a process comprising contacting a sulfided catalyst consisting of one of the metals tungsten, chromium, or molybdenum and one of the metals nickel, cobalt, or iron supported upon a carrier metal having a minimum cracking activity equivalent to a rating of 14.1 per cent on the Kellogg scale, with a stream of liquid deasphalted hydrocarbon charge oil in admixture with a stream of hydrogen under hydrogenation conditions of temperature of 343°C to 441°C, a pressure of 105 kilograms per square centimetre gauge to 700 kilograms per square centimetre gauge, a space velocity of 0.25 to 2.0 liquid volumes of hydrocarbon charge per hour per volume of catalyst, and a hydrogen rate of 56 to 420 standard cubic metres of hydrogen per barrel of charge oil, wherein the catalyst may comprise a total of from 5 to 40% of the said metals by weight of the total catalyst weight, and the atomic ratio of the metal(s) nickel, cobalt or iron to the metal(s) tungsten, chromium, or molybdenum may be from 0.1:1 to 5:1.
- Also, it previously has been proposed in our British Patent Specification No. 928,762 to provide a catalyst composition for use in the catalytic hydrogenation of hydrocarbons comprising halogen-containing sulfided nickel and tungsten disposed upon a supporting material having an activity for cracking corresponding to a rating of at least 14.1 per cent on the Kellogg activity scale, the total weight of said nickel and tungsten being 5 per cent to 40 per cent of the total composition weight, the amount of halogen being between 0.4 and 6 per cent of the total catalyst weight, the total weight of sulfur being 2 per cent to 23 per cent of the total catalyst weight, and the atomic ratio of said tungsten to nickel being between 1 and 0.1 and 1 to 5.
- While the yields, viscosity indicates and iodine numbers of liquid deasphalted hydrocarbon charge oils treated by these prior processes and catalysts have been adequate, it is an object of the present invention to improve thereon.
- There has been discovered, in accordance with this invention, an improved process for the upgrading of crude lubricating oil stocks employing an improved catalyst whereby greater yields of enhanced lubricating oils are obtained which have a higher viscosity index and a lower iodine number than obtained with

2 previously suggested processes and catalysts. This is achieved by the use of a catalyst containing optionally in place of or in addition to a group VI and a group VIII metal or a sulfide thereof, an oxide thereof, supported on an alumina carrier, the total metals content as hereinafter defined being at least 20% by weight based on the total catalyst weight, and the atomic ratio of group VIII metals to group VI metals being in the range from 2.25:1 to 6:1.

5 Therefore, in accordance with this invention, there is provided a process for enhancing lubricating oils, wherein a crude lubricating oil stock is contacted with hydrogen under hydro-  
15 genating conditions of elevated temperature and pressure in the presence of a catalyst comprising at least one group VI or an oxide or sulfide thereof together with at least one group VIII metal or an oxide or sulfide thereof, supported on an alumina carrier and containing a halogen, the total metals content of this catalyst constituting at least 20 per cent by weight of the total catalyst and the group VI and VIII metals being present in an atomic ratio of group VIII metals to group VI metals in the range from 2.25:1 to 6:1.

25 Further, according to the present invention there is provided a catalyst for use in the process aforesaid, including at least one of the group VI metals, or an oxide or sulfide thereof, and at least one of the group VIII metals, or an oxide or sulfide thereof, supported on an alumina carrier and containing a halogen, the total metals content as hereinafter defined constituting at least 20 per cent by weight based on the total catalyst and the atomic ratio of group VIII metals to group VI metals being in the range from 2.25:1 to 6:1.

40 The term "total metals content" as used herein and in the claims is to be understood to exclude aluminium in the alumina carrier.

45 It is essential that the catalysts of this invention have a total metals content of at least 20 per cent and preferably have a total metals content from 30 per cent to 50 per cent by weight based on the total catalyst. It is also essential that the Group VI and VIII metals employed in the catalyst of this invention are present in the ratios mentioned above. It is preferred, however, to employ catalysts wherein the atomic ratio of Group VIII metals to Group VI metals is in the range from 2.5:1 to 5.0:1. It has been found that catalysts containing both Group VI and VIII metals in ratios other than that required by the catalyst of this invention, although having a total metals content within the range specified for the catalyst of this invention, are not effective to produce the advantageous results obtained in accordance with this invention. Similarly, it has been found that catalysts containing Group VI and VIII metals within the ranges of atomic ratios required by this invention but  
65 having a total metals content outside the range

of the catalysts of this invention also fail to produce the advantageous results obtained in accordance with this invention. Thus, it is essential that the catalyst of this invention have both the total metals content mentioned above as well as having Group VI and VIII metals present in the ratios mentioned previously. It is also essential that the catalyst of this invention contain a combined halogen, usually in an amount from 0.5 per cent to 10.0 per cent by weight of the total catalyst and preferably from 1.0 to 4.0 per cent by weight.

70 The metalliferous components of the catalyst of this invention may comprise any one or more of the Group VI metals together with any one or more of the Group VIII metals. Normally, the metals employed will be the chromium, molybdenum or tungsten metals of Group VI and the iron group metals of Group VIII, i.e. iron, cobalt, or nickel. As mentioned previously, these metalliferous components can be employed either as the metals themselves or as the oxides or sulfides of such metals. It is preferred, however, to employ the sulfides of the Group VI and VIII metals. A particularly preferred method of operation comprises employing a catalyst wherein the metalliferous components are initially in a substantially unsulfided state such as, for example, a reduced metal state, the oxide of the metal or wherein the metals are only partially sulfided, and then sulfiding the metalliferous components *in situ*, preferably during the start-up of the hydrogen treating process. It has also been found that particularly good results are obtained when employing combinations of nickel, cobalt and molybdenum; nickel and molybdenum; cobalt and molybdenum; and especially nickel and tungsten.

105 The carrier employed in this invention must be alumina which material normally has low activity for the promotion of cracking. Generally, it will be found that such aluminas have a cracking activity index below about 35 and even below about 30. A preferred carrier has an activity index of about 18.

110 The catalyst of this invention can be prepared employing any of the techniques for the preparation of multi-component catalysts well known in the art. Thus, for example, the catalyst can be prepared by impregnating the calcined alumina employing a solution of the salts of the metals as well as the halogen. Generally, one impregnation step is sufficient to provide a catalyst containing up to about 25 per cent and sometimes even 30 per cent total metals content. However, for catalysts containing a greater metals content than this, particularly the catalysts containing 40 per cent or more metals or more, it has been found that two or more impregnation steps are necessary. When employing multiple impregnation steps, the catalyst is dried and calcined in between impregnations.

The crude lubricating oil stocks treated in accordance with the process of this invention can be of the type well-known in the art which stocks boil generally in the gas oil or heavy gas oil range and above. Thus, for example, such crude lubricating oil stocks usually boil predominantly above about 316° or 343°C. and include stocks ranging from light distillates to untreated residues obtained from vacuum or atmospheric towers. It has been found that the process of this invention is particularly effective in the treatment of crude lubricating oil stocks which have been obtained from a residual material which has been treated so as to lower the sulfur, nitrogen, and asphaltene contents to a level below that of the original residue, including residual stocks which have been deasphalted employing a light paraffinic solvent. The process of this invention is also particularly suitable for the treatment of stocks which have been treated for the reduction of aromatic content, such as, for example, the raffinates from solvent extraction processes including a raffinate from a Duo-Sol treatment.

While the catalyst and process of this invention are suitable to obtain products having viscosity indices varying over a wide range, it has been found that the catalyst and process are particularly suitable when a product having a comparatively high viscosity index is desired. Thus, the catalyst and process of this invention can be advantageously employed to yield a product having a viscosity index in the range from about 120 or 125 up to about 140 or even higher.

In conducting the process of this invention, a temperature is employed in the range from 316° to 480°C. and preferably from 371° to 427°C., a pressure in the range from 70 to 350 and preferably from 140 to 210 kilograms per square centimetre gauge, a liquid hourly space velocity from 0.1 to 10.0 volumes of crude lubricating oil stock per volume of catalyst per hour and a hydrogen feed rate from 35.6 to 356 standard cubic metres of hydrogen per 100 litres of crude lubricating oil stock, preferably from 71.2 to 178 standard cubic metres of hydrogen per 100 litres of crude lubricating oil stock. It is not necessary that pure hydrogen be employed in the process of this invention and a hydrogen containing stream comprising from 60 per cent to 99 per cent hydrogen is satisfactory. Normally, the

hydrogen containing streams generally available in refinery operations containing from 85 per cent to 90 per cent hydrogen can be used.

In the following Examples I to III two different commercially available materials were employed as carriers in the catalyst compositions. One of these supports comprised about 75 per cent silica and about 25 per cent alumina. This silica-alumina composition is commercially available from American Cyanamid Company under the trade name of "Aerocat Triple A High Alumina Cracking Catalyst". Representative samples of this composition have an average cracking Activity Index of about 76. The other support is comprised substantially entirely of alumina commercially available from the Harshaw Chemical Company under the trade name of "Al-1706". This material has an Activity Index of 18. In the preparation of the catalysts, each of these materials, both the silica-alumina and the alumina, were sized to 10—20 mesh (.84 to 2 millimetre sieve openings) and calcined at 538°C. for ten hours. This was followed by impregnation with an aqueous solution of ammonium metatungstate and nickel nitrate. In those catalysts containing fluoride the impregnation solution also contained ammonium fluoride. The proportions of ammonium metatungstate and nickel nitrate employed in the individual impregnation steps were varied so as to provide finished, impregnated catalysts with the desired ratios of nickel and tungsten. For the catalysts containing up to 30 per cent by weight total metals content, one impregnation step was sufficient. For the catalysts containing higher total metals contents than this, two impregnations were required. The catalysts subjected to two impregnations were oven dried at 121°C. and calcined at 538°C. for about ten hours between impregnations. After impregnation to deposit the total metals desired, all of the catalysts were oven dried at 121°C. for 24 hours and calcined at 538°C. for ten hours. Prior to employment in the examples, the catalysts were sulfided with a 10 per cent H<sub>2</sub>S—90 per cent hydrogen gas stream, (1890 STP space velocity) for eight hours at 316°C. and atmospheric pressure.

#### EXAMPLE I

In this example a Duo-Sol raffinate having the inspections shown in Table I below was employed as the charge stock.

TABLE I

Gravity: °API	29.7
Viscosity, SUV: Sec.	171
66°C.	71.2
99°C.	110
Viscosity Index	32
Pour Point: °C. (D 97)	L 5.5
Colour, D 1500	0.12
Sulfur, % by Wt.	8.0
Iodine No.	9.3
Aromatics, % by Wt.	90.7
Saturates, % by Wt.	0.019
Total Nitrogen, % by Wt.	37
Basic Nitrogen, PPM	

5 This charge stock was processed at a pressure of 157.5 kilograms per square centimetre gauge, a liquid hourly space velocity of 1.5 and at temperatures in the range from 375° to about 429°C. in separate runs employing

different catalysts in different runs. The particular proportions of metals in each of the catalysts and the supports employed in the catalysts along with yield data is shown in Table II below. 10

TABLE II

Catalytic Metals % by Wt.	Total Metals, % by Wt.	Support	Ni to W, (Wt. Ratio)	Ni to W (Atomic Ratio)	99°C. Vis at 125 VI (SUS)	Yield at 125 VI (% by Vol. of Charge)	Temperature Required for 125 VI (°C.)
20% Ni—20% W	40	Alumina	1.0	3.13	55.2	86	388
10% Ni—10% W	20	Alumina	1.0	1.13	54.7	85	406
30% Ni—20% W	50	Alumina	1.5	4.70	53.0	85	394
20% Ni—30% W	50	Alumina	0.67	2.09	53.0	77	389
30% Ni—10% W	40	Alumina	3.0	9.40	51.5	76	408
6% Ni—19% W	25	Alumina	0.3	0.99	51.5	75	412
20% Ni—10% W	30	Alumina	2.0	6.27	51.0	77	414
6% Ni—19% W	25	Silica-Alumina	0.3	0.99	—	62	382
20% Ni—20% W	40	Silica-Alumina	1.0	3.13	—	62	387

All of the above catalysts with the exception of the 20% nickel—20% tungsten on silica-alumina contained 2% fluorine.

From the data in Table II above it will be seen that the first three catalysts of Table II each contained more than 20 per cent by weight of total metals and that the atomic ratios of Group VIII metal to Group VI metal of these catalysts were all within the range preferred in this invention, namely, from 2.5:1 to 5.0:1, and that in each of the runs employing these catalysts the yield of 125 VI product obtained was at least about 10 per cent higher than the yields obtained in the runs employing other catalysts. It is significant to note that various other catalysts containing from 25 to 40 per cent total metals content but having a ratio of Group VIII to Group VI metals outside the range required by this present invention failed to produce the superior results obtained in accordance with this invention.

Illustrative of the superior results obtained in accordance with this invention process throughout the range of operation described above are the data graphically illustrated in Figures 1 to 3 of the accompanying drawings wherein:

Figure 1 is a plot of the yield of 371°C. + nondewaxed product (per cent by volume of charge) versus temperature required;

Figure 2 is a plot of the yield of 371°C. + nondewaxed product (per cent by volume of charge) versus the VI of the nondewaxed product; and

Figure 3 is a plot of the yield of 371°C. + dewaxed product (per cent by volume of charge) versus the VI of such product.

In Figures 1 and 2 the results obtained when employing a 20% nickel—20% tungsten on alumina catalyst of the present invention are shown as well as the results obtained when employing the same ratio of metals in a 20% nickel—20% tungsten on silica-alumina catalyst as well as a 6% nickel—19% tungsten—2% fluorine on silica-alumina catalyst representative of prior art catalysts. (In all of the figures of the attached drawings the same catalyst is indicated by the same symbol; thus, the triangle indicates the 20% nickel—20% tungsten—2% fluorine on  $Al_2O_3$  cata-

lyst, the circle indicates the 6% nickel—19% tungsten—2% fluorine on  $SiO_2-Al_2O_3$  catalyst, in Figures 1 and 2 the square indicates the 20% nickel—20% tungsten on  $SiO_2-Al_2O_3$  catalyst, and in Figures 4 and 5, described hereinafter, the diamond indicates a 20% nickel—10% molybdenum—2% fluorine on  $Al_2O_3$  catalyst). By referring to Figure 1 it will be seen that the 20% nickel—20% tungsten catalyst of this invention provided an increase in yield ranging from about 20 per cent up to about 40 per cent throughout the range from about 371° to about 429°C. Figure 2 illustrates that the process of the present invention employing a 20% nickel—20% tungsten on alumina catalyst not only provided an increase in yield in the range from about 20 per cent to about 35 per cent for any particular VI product, but also demonstrates that a viscosity index improvement of about 15 or more can be obtained at any particular level of yield over that obtained with either the 20% nickel—20% tungsten on silica-alumina catalyst or the 6% nickel—19% tungsten catalyst. Figure 3 illustrates that substantially the same advantage in yield exists between the dewaxed products obtained using the 20% nickel—20% tungsten on alumina catalyst of this invention as opposed to the 6% nickel—19% tungsten—2% fluorine on silica-alumina of the prior art.

#### EXAMPLE II

In this example samples of the nondewaxed lubricating oils obtained at various operating temperatures employed in Example I utilizing the 6% nickel, 19% tungsten and 2% fluorine on silica-alumina catalyst and the 20% nickel, 20% tungsten and 2% fluorine on alumina catalyst were tested for color stability. The ASTM D 150 color for each of the samples obtained at the temperatures indicated in Table III below was initially determined. These samples were then exposed to sunlight for a period of 49 days and, again, the ASTM D 1500 color for each of the samples was determined. These data are shown in Table III below.

TABLE III

Catalyst	Initial Color	Color after 49 Days in Sunlight
6% Ni—19% W—2% F on Silica-Alumina	<1.5	3.5
375°C.	<1.5	3.5
387°C.	<1.5	3.5
399°C.		
20% Ni—20% W—20% F on Alumina	<1.0	1.5
382°C.	<1.0	1.5
405°C.		

From the above data it will be noted that the products obtained in accordance with this invention and employing the 20% nickel—20% tungsten on alumina catalyst initially had a color somewhat lower than the lubricating oils obtained employing a prior art catalyst. Most significantly, however, it will be noticed that the lubricating oils produced in accordance with this invention have a much greater color stability, showing only very slight increase in color during the 49-day test period, than the lubricating oils obtained with the prior art technique, which oils evidenced a substantial increase in color.

#### EXAMPLE III

In this example, the same Duo-Sol raffinate

as employed in Example I was subjected to hydro-treatment under conditions substantially the same as those employed in Example I including a liquid hourly space velocity of 1.5, a pressure of 157.5 kilograms per square centimetre gauge and temperatures in the range from about 371° up to about 429° C. Separate runs were conducted employing two different catalysts, one containing 20% nickel, 20% tungsten and no fluorine on an alumina support while the other catalyst contained 20% nickel, 20% tungsten and 2% fluorine. The following Table IV shows the iodine number and the viscosity index of the nondewaxed products obtained at the nominal temperatures of 382°, 404° and 429°C.

TABLE IV

	Iodine Number		Viscosity Index	
	0% F	2% F	0% F	2% F
382°C.	2.6	1.6	108	122
404°C.	2.9	1.8	121	134
429°C.	3.0	1.9	138	148

The data in Table IV above clearly indicate that the employment of a catalyst of this invention containing combined halogen is necessary to effect sufficient hydrogenation so as to provide a product having a sufficiently low iodine number, i.e. below about 2.0, and that such catalyst is effective to produce a

product having a viscosity index of substantially higher value than obtained with a similar catalyst but not containing combined halogen.

#### EXAMPLE IV

In this example, a deasphalted Ordovician residuum having the inspections shown in Table V below was employed as the charge stock.

TABLE V

Gravity: °API	23.8
Viscosity, SUV: Sec.	
66°C.	581
99°C.	158
Viscosity Index	91
Pour Point: °C. (D 97)	24
Color, D 1500	dil. 4.0
Sulfur, % by Wt.	0.23
Iodine No.	12.2
Aromatics, % by Wt.	44.0
Saturates, % by Wt.	56.0
Total Nitrogen, % by Wt.	0.063
Basic Nitrogen, PPM	265

This charge stock was processed at a pressure of 210 kilograms per square centimetre gauge, a liquid hourly space velocity of 0.5 and at temperatures in the range from 371° to about 416°C. in separate runs employing different catalysts in each run. The particular catalysts employed were the 20% nickel, 20% tungsten and 2% fluorine on alumina catalyst of this invention, the prior art 6% nickel, 19% tungsten and 2% fluorine on silica-alumina catalyst, both of which were described in the previous examples, and two nickel and molybdenum on alumina catalysts. One of these nickel and molybdenum catalysts contained 20% by weight nickel, 20% by weight molybdenum and 2% by weight fluorine on the commercially available alumina described previously while the other contained 20% by weight nickel, 10% by weight molybdenum and 2% by weight fluorine on the alumina described above. In the 20% nickel—20% molybdenum catalyst the atomic ratio of nickel to molybdenum is about 1.64:1, which is outside the range required in accordance with this invention, but the atomic ratio of nickel to molybdenum in the 20% nickel—10% molybdenum catalyst is about 3.28:1, which is within the range required by this invention. These nickel and molybdenum catalysts were prepared in substantially the same manner set forth above regarding the nickel and tungsten catalysts. The metal containing compounds employed in the impregnating solution were nickel nitrate and ammonium molybdate and multiple impregnations were required in the preparation of both catalysts. From the data obtained in these runs, a series of graphs were plotted illustrating the superior results obtained in accordance with this process employing the catalysts of this invention throughout the range of operation described above. These graphs are shown in Figures 4 to 8 of the attached drawings wherein:

Figure 4 is a plot of the yield of 385°C. + nondewaxed product (% by volume of charge) versus the temperature required;

Figure 5 is a plot of the yield of 385°C. + nondewaxed product (% by volume of charge) versus the VI of the product;

Figure 6 is a plot of the viscosity of the nondewaxed product at 38°C. versus the VI of the product;

Figure 7 is a plot of the viscosity of the nondewaxed product at 99°C. versus the VI of the product; and

Figure 8 is a plot of the iodine number of the product versus the temperature employed.

The results obtained when employing the 20% nickel—20% molybdenum catalyst, not a catalyst of this invention, were not significantly different from the results obtained when employing the prior art 6% nickel—19% tungsten on silica-alumina catalyst. This was particularly so in the range of products having

a viscosity index of 125 or greater. Thus, the yield of 385°C. + nondewaxed product having a VI of 125 was 59%, only about 2% greater than obtained with the prior art catalyst, and the yield of 129 VI product was 45%, about 3% less than obtained with the 6% nickel—19% tungsten catalyst. In order not to clutter the figures of the drawings with plots of data which are merely cumulative to other data, the data obtained employing the 20% nickel—20% molybdenum catalyst have not been plotted.

Referring now to Figure 4, it will be seen that when operating in accordance with this invention and employing the 20% nickel—20% tungsten on alumina catalyst, yields were obtained which ranged from about 10 per cent to more than 40 per cent greater than the yields obtained when employing a prior art catalyst such as the 6% nickel—19% tungsten on silica-alumina. Similarly, it will be noticed that the 20% nickel—10% molybdenum catalyst of this invention provided yields which ranged from about 15 per cent to more than 50 per cent greater than the yields obtained with the prior art 6% nickel—19% tungsten catalyst. Not only does the process of this invention provide a substantial increase in yield over that obtained with prior art techniques, but by referring to Figure 5 it will be seen that the process of this invention also provides a greater yield of product having a substantially higher viscosity index than obtained in accordance with previously suggested techniques.

The plot of the data in Figures 6 and 7 clearly illustrates that when treating a comparatively heavy charge stock, such as the deasphalted residuum of this example, the process of this invention yields products having viscosity indices greater than about 115 or 120 which have a somewhat higher viscosity, both at 38°C. and 99°C. than obtained with a representative prior art catalyst. It will be realized that production of heavier oils at a given VI is particularly advantageous since high VI oils produced by hydrogen treatment often have viscosities too low to meet specifications for a multi-viscosity oil, e.g. SAE 10W/30 lube oil.

Finally, the plot of the data shown in Figure 8 illustrates that the process of this invention is effective to produce a product having an iodine number somewhat lower than was obtained with a prior art catalyst and substantially below 2.0.

#### EXAMPLE V

In this example, a blend of the deasphalted Ordovician residuum of Example IV and Ordovician lube distillates with 4 ppm of added ortho-fluorotoluene was employed as the charge stock. This blend had an API gravity of 25.8°, an iodine number of 15.7, a viscosity SUS at 99° C. of 64.1 and a viscosity index of 100. The catalyst employed was sub-



stantially the same as the 20% nickel—20% tungsten—2% fluorine on alumina catalyst employed in Examples I through IV, with the exception that the catalyst of this example was not presulfided. The initial operating conditions employed included a temperature of 394°C., a gas recycle rate of 89 standard cubic metres per 100 litres, a total pressure of 210 kilograms per square centimetre gauge and a minimum hydrogen partial pressure of 157.5 kilograms per square centimetre. These initial conditions were maintained for a period of three weeks to produce a 116 to 118 VI product (estimated to be 108 to 110 VI dewaxed). During this three week period no deactivation of the catalyst was detected.

In order to accelerate aging the temperature was increased to 406°C. which yielded a 121 to 125 VI nondewaxed product. This temperature increase also resulted in an increase in API gravity of the product from 30.4° API to 31.8° API. Simultaneously, a decrease in iodine number of about 1 was detected in the product compared to that obtained at 394°C. During the ensuing four weeks, a temperature increase of 2°C. (from 406°C. to 408°C.) was necessary in order to maintain the 121 to 125 VI product. This represented an increase of only about .5°C. per week, thereby indicating that reasonably long catalyst life can be anticipated. After seven weeks, a check period of about one week operation at the initial 394°C. starting temperature showed that a loss of about 3 VI had occurred in the product representing an overall deactivation for the total period of about 4°C. or about .5°C. per week.

#### WHAT WE CLAIM IS:—

1. An improved process for enhancing lubricating oils, which comprises contacting a crude lubricating oil stock with hydrogen under hydrogenating conditions including an elevated temperature and pressure, in the presence of a catalyst comprising at least one of the Group VI metals, or an oxide or sulfide thereof, and at least one of the Group VIII metals, or an oxide or sulfide thereof, supported on an alumina carrier and containing a halogen, the total metals content as hereinbefore defined constituting at least 20 per cent by weight based on the total catalyst and the Group VI and VIII metals being present in an atomic ratio of Group VIII metals to Group VI metals in the range from 2.25:1 to 6:1.

2. A process according to claim 1, wherein the total metals content of the catalyst is from 30 per cent to 50 per cent by weight based on the total catalyst.

3. A process according to claim 1 or claim

2, wherein the atomic ratio of Group VIII metals to Group VI metals is in the range from 2.5:1 to 5.0:1.

4. A process according to any one of the preceding claims, wherein the halogen is fluorine and it is present in an amount from 0.5 per cent to 10.0 per cent by weight based on the total catalyst.

5. A process according to any one of the preceding claims, wherein the Group VI metal is tungsten and the Group VIII metal is nickel.

6. A process according to any one of the preceding claims, wherein the crude lubricating oil stock is a deasphalted residuum.

7. A process according to any one of the preceding claims, wherein the contacting is conducted at a temperature in the range from 316° to 480°C., a pressure in the range from 70 to 350 kilograms per square centimetre gauge, a liquid hourly space velocity in the range from 0.1 to 10.0 and a hydrogen feed rate in the range from 35.6 to 356 standard cubic metres of hydrogen per 100 litres of crude lubricating oil stock.

8. An improved catalyst for use in the process claimed in any one of claims 1 to 7, comprising at least one of the Group VI metals, or an oxide or sulfide thereof, and at least one of the Group VIII metals, or an oxide or sulfide thereof, supported on an alumina carrier and containing a halogen, the total metals content as hereinbefore defined constituting at least 20 per cent by weight based on the total catalyst and the atomic ratio of Group VIII metals to Group VI metals being in the range from 2.25:1 to 6:1.

9. A catalyst as claimed in claim 8, wherein the total metals content is from 30 per cent to 50 percent by weight and the halogen is present in an amount from 0.5 to 10.0 per cent by weight, all based on the total catalyst.

10. A catalyst as claimed in claim 8 or claim 9, wherein the Group VI metal is tungsten and the Group VIII metal is nickel and the atomic ratio of Group VIII metal to Group VI metal is in the range from 2.5:1 to 5.0:1.

11. An improved process according to claim 1 for enhancing lubricating oils, substantially as hereinbefore described, or according to any one of the Examples.

12. A lubricating oil prepared by the process claimed in any one of claims 1 to 7 or claim 11.

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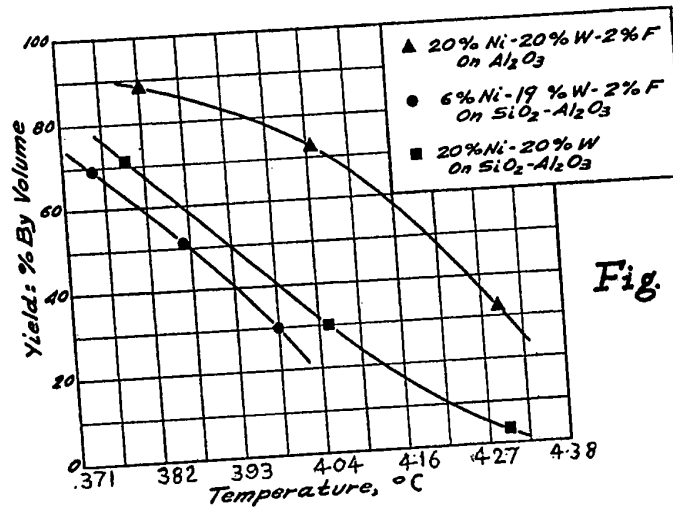


Fig. 1

Fig. 2

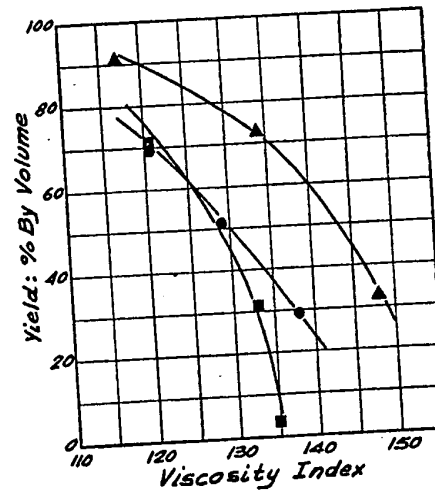


Fig. 3

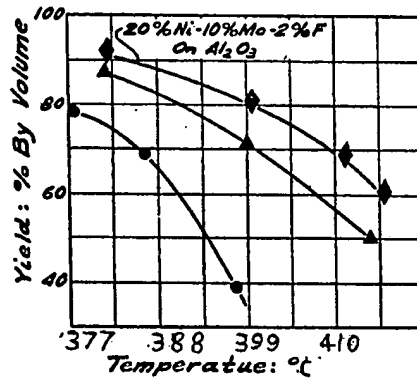
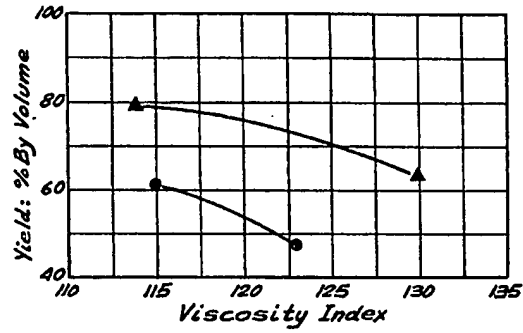
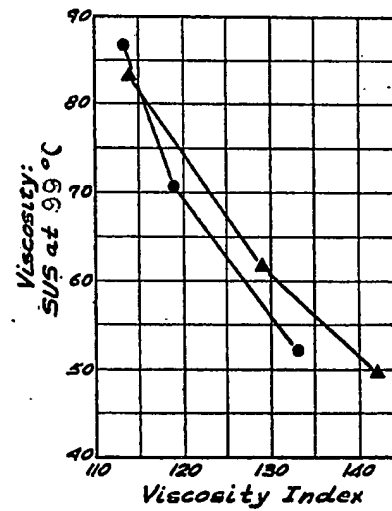


Fig. 4

Fig. 7



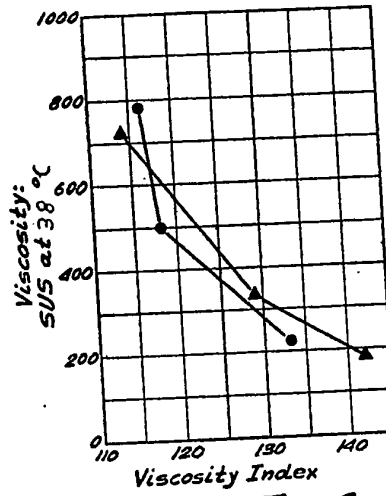


Fig. 6

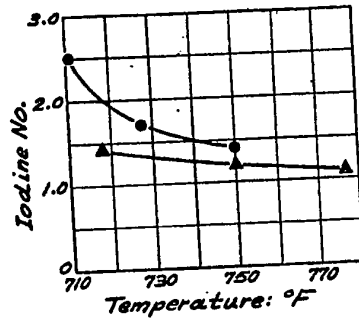


Fig. 8

Fig. 5

